

# ROLE OF ON-LINE MASS SPECTROMETRY FOR STUDYING THE STRUCTURE/REACTIVITY RELATIONSHIPS AND CONVERSION PROCESSES OF COAL

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## INTRODUCTION

Less than two decades ago a typical mass spectrometer was an extremely expensive and delicate instrument that would completely take up a moderately sized laboratory room. Few coal scientists or engineers had access to such an instrument and even fewer mass spectrometrists were willing to "contaminate" their instrument with something as complex and dirty as coal and its tar. Against this historic background it is nothing less than amazing that as early as 1966 Vastola et al. [1] at Penn State University, using a finely focussed ruby laser and a time of flight (TOF) mass spectrometer, already carried out laser pyrolysis experiments on coal samples inside the ion source. Their example was soon followed by Joy et al., [2]. However, since Vastola's experiment was too far ahead of the state-of-the-art in signal processing electronics it would take more than 15 years before his group was able to obtain reproducible pyrolysis mass spectrometry (Py-MS) patterns from a series of PSOC coal samples [3].

In the meantime, the same coal samples had already been studied by Curie-point pyrolysis mass spectrometry (Py-MS) in our own laboratory [4] as part of a series of 104 Rocky Mountain Province coals. The latter study demonstrated the reproducibility of carefully designed, dedicated Py-MS instruments, as well as the power of multivariate statistical analysis techniques, for reducing the voluminous MS data and bringing out the most significant chemical components and trends.

Already during the late seventies and early eighties several organic geochemistry groups, e.g., at the Technical University Delft (DeLeeuw et al. [5]) at Chevron (Gallegos [6]) and at the University of Bartlesville (Philp et al. [7]) had started to use pyrolysis-gas chromatography/mass spectrometry to characterize a broad range of different coals and coal macerals. Yet another promising instrumental approach, namely thermogravimetry (TG) in direct combination with MS (also reported by Gallegos [6]) was being developed further by Szekely's laboratory in Budapest [8] followed by the development of a vacuum TG/MS system in our own laboratory (Yun [9]). In the mid eighties further advances in TG/MS techniques were reported by Ohrbaech and Kettrup [10] using a commercially available molecular beam type interface. Most recently, a homebuilt TG/MS system based on similar principles was successfully tested in our own laboratory [11]. Finally, the promising results of the various TG/MS combinations prompted us to pursue more sophisticated analytical configurations such as TG/IR/MS [12] and TG/GC/MS [13], with the latter method eventually being adapted to on-line analysis of high pressure reactions, as reported by Kui et al. [14].

In the mid eighties, Schulten's laboratory in West Germany started pursuing an entirely different approach involving direct probe type pyrolysis of coal directly in the ion source of a high resolution magnetic sector MS system with field ionization (FI) and field desorption (FD) capabilities [15]. Related FIMS work was reported at SRI by Malhotra et al. [16]. That a wealth of information on coal conversion processes and reaction products could also be obtained by high resolution MS in combination with other ionization methods, such as low voltage electron ionization (LVEI) and fast atom bombardment (FAB) was elegantly demonstrated by Winans et al. [17] at Argonne National Laboratory. Last year, a collaborative comparison between different desorption/ionization methods capable of producing ion signals up to several thousand Dalton was performed by two different research groups [18]. Barely was their report submitted or one of the authors (Herod, et al.) published several articles raising the upper mass limit of detected ion species to 4,000 and 270,000 Dalton for FAB [19] and matrix assisted laser desorption/ionization (MALDI [20]), respectively.

Obviously, high mass MS techniques are presently a hot topic in coal science. However, in order to keep the scope of this article within the limitations posed by the ACS Fuel Chemistry Division preprint format, only techniques and applications of MS methods involving direct coupling to micro-scale or upscale coal conversion reactors will be discussed.

## METHODOLOGY

Figure 1 depicts six basic configurations that have found application in coal science and technology. Sequentially progressing from configuration I to configuration VI we notice an increasing spatial and temporal separation between reaction and ionization zones. Configurations I-III involve vacuum pyrolysis. However, whereas in configuration I reaction and ionization zones overlap more or less completely, configurations II and III require some vapor transport mechanism. Configurations IV and V feature (near)ambient pressure reactors whereas configuration VI depicts a high pressure reactor. The degree of separation between reaction and ionization regions in configurations IV and V progresses from a molecular beam or leak type inlet (IV) to a capillary transfer line or full fledged chromatographic column (V). The final configuration (VI) shows a high pressure reactor region with a two stage coupling (involving an intermediate ambient pressure step) to the mass spectrometer vacuum.

Configuration I - Integral Pyrolysis/Ionization Zones - Examples include the LAMMA (Laser Microprobe Mass Analyzer) experiments (Dutta and Talmi [21]) and the pyrolysis field desorption MS studies (Schulten [22]) reported in 1982. Also some of the early laser ionization MS experiments reported by Vastola et al. [23] and Joy et al. [2] fall into this category. More recently, FAB studies were described by Winans et al. [24] and by Herod et al. [19] whereas laser desorption/ionization experiments were reported by Herod et al. [25] and by John et al. [20]. Generally speaking, the interpretation of the results obtained by the integral degradation/desorption/ionization methods have two things in common: (1) very large ions (ranging from  $10^3$  to over  $10^5$  Daltons) are observed, and (2) chemical interpretation of the results has not yet been very successful.

Configuration II - Direct Probe Inlets - Much of the published on-line MS work falls under this broad category, which includes direct probe Py-FIMS, as well as Curie-point Py-MS and vacuum TG/MS studies. Also, the newer work reported by Vastola's group, involving LVEIMS of neutral laser pyrolysis products, falls under this category. As shown in Figure 2 results obtained by the various techniques can be surprisingly similar in spite of the large differences in pyrolysis, ionization and mass spectrometry methods used. This demonstrates that the underlying pyrolysis chemistry is quite constant and that a satisfactory degree of interlaboratory reproducibility is attainable when operating under chemically controlled, conditions (as is readily achievable in Configuration II experiments). Among these techniques, the pyrolysis field ionization MS results reported by the German [26] and US groups [16] stand out with regard to mass range covered (up to approx. 1200 amu) and the absence of confusing fragmentation processes such as produced by conventional (70 eV) electron ionization. However, the upper mass range limit in Py-FIMS is determined by vapor transport limitations and ion transmission characteristics of the mass spectrometer. Remarkably similar spectra can be obtained by electron ionization at 12 eV, as reported by Taghizadeh et al. [27] and Yun et al. [28] and illustrated in Figure 2. As illustrated in Figure 3, the work performed with configuration II instruments has distinguished itself with regard to the application of advanced data reduction and pattern recognition methods [4, 29], especially when combined with time- and temperature-resolved MS data [30, 31].

Configuration III - Vacuum Manifold Inlets - The use of vacuum manifold type transfer lines between pyrolysis and ionization regions is generally the result of MS instruments equipped with batch (vapor) inlets being adapted to pyrolysis studies. Some of the work reported by Winans et al. [32] and by Burnham et al. [33] falls into this category. Also, Curie-point Py-MS studies using a so-called "expansion chamber" [34,35] could be included here. With properly heated, inactivated lines and short residence times results of vacuum manifold type inlets may become "nearly indistinguishable from category II direct probe inlet results. However, the risk of desorption losses and/or secondary reactions requires careful attention to experimental procedures.

Configuration IV - Molecular Beam Type Interfaces - The commercial TG/MS system used by Ohrbach and Ketrupp [10] has an inlet consisting of two nested quartz tubes with carefully aligned centerline pinholes, affording direct access of volatile products into the ion source of a quadrupole mass spectrometer. Nonetheless, the largest coal pyrolysis product ions reported by these authors appear to consist of relatively low MW phenols. A more recent inlet of this type developed by Nie et al. [11] features special flow arrangements designed to minimize condensation losses and the low voltage EI MS patterns obtained closely resemble the corresponding Py-FIMS profiles produced with configuration II type inlets, with peak intensities well into the  $m/z$  400-500 range.

Configuration V - Transfer Line and GC Column Interfaces - Configurations falling into this category feature a narrow bore capillary transfer line which may or may not function as a GC column, depending on temperature and sample injection method used. A broad variety of Py-GC/MS type inlets have been used to study the organic geochemistry of coal and coal macerals

[36]. Closely related is the so-called transfer line GC (TLGC) interface between reaction and pyrolysis zone described by Maswadeh et al [37] for CO<sub>2</sub> laser pyrolysis studies of single coal particles (see GC/MS profiles in Figure 4). Furthermore, the capillary TG/MS interface used by Blaszo et al. [8] and the TG/IR/MS interface reported by our laboratory [12] could be included here, as well as the recent ruby laser Py-GC/MS studies reported by Greenwood et al. [38].

Configuration VI - High Pressure Transfer Line GC Interfaces - Most recently, Kiu et al. [14] described a two stage TLGC interface between a high pressure PG system and a quadrupole mass spectrometer permitting on-line monitoring of high pressure (hydro) pyrolysis reactions in coal under thermally and catalytically controlled conditions. Currently, work is underway in our laboratory to extend this approach to high pressure liquid flow-through reactors [39], thus permitting monitoring of coal hydroliquefaction processes, as illustrated in Figure 5.

## APPLICATIONS

Fortunately, the bewildering array of techniques described appears to conceal a limited number of experimental objectives, namely: (A) elucidation of coal composition and structure as well as structure/reactivity relationships; (B) mechanistic and kinetic studies of coal reactions and (C) optimization of coal conversion processes as well as a characterization of conversion products.

(A) Structural Characterization - This includes many of the organic geochemistry studies using type V (Py-GC/MS) inlet configurations as well as the type I desorption/ionization experiments by means of laser, fast atom bombardment or field desorption techniques. Most recently John et al. reported the "identification" of molecular masses up to 270,000 Dalton by Matrix-Assisted laser desorption MS [20]. Major contributions in this area have also been made by direct probe type (Configuration II) pyrolysis FIMS and HRFIMS studies and by the vacuum manifold (Configuration III) type HREIMS work shown in Figure 6. It can be stated without exaggeration that our current understanding of the molecular composition and structure of coal and its structure/reactivity relationships, however incomplete, depends more strongly on mass spectrometry than on any other analytical methodology.

(B) Reaction Mechanisms and Kinetics - Particularly informative are the time- and temperature-resolved pyrolysis MS studies performed with category II (see Figure 7) as well as IV type experiments which combine the ability to detect labile, reactive species while permitting quantitative analysis of rates and yields. Combined thermogravimetry/mass spectrometry methods are especially well suited for such studies since knowledge of the precise weight loss rates and yields without knowing the chemical identity of the reactive species involved, and *vice versa*, does not fulfill the elementary criteria for kinetic and mechanistic studies. Nevertheless, useful information has been contributed by type III (e.g., HRMS) and type IV (e.g., laser Py-GC/MS) configurations, whereas type VI (high pressure TLGC/MS) methods are starting to open up a whole new field of study for catalytic reaction mechanisms and kinetics.

(C) Conversion Process and Product Characterization - Field Ionization MS techniques have gained an especially strong reputation in this area, although it should be pointed out that measurable vapor pressures are a strict requirement. Completely nonvolatile conversion products can only be analyzed by means of category I desorption/ionization techniques, although generally in an off-line mode. Sufficiently volatile conversion products can, of course, be analyzed by category V (or VI) on-line GC/MS techniques. Due to the availability of MS reference libraries containing over 200,000 standard spectra GC/MS techniques are likely to remain unparalleled in their ability to provide positive chemical identification of compounds in complex mixtures. For dynamic processes type IV molecular beam inlets offer a superior solution. However, if positive chemical identification is required short column "transfer line" GC methods may be the best compromise.

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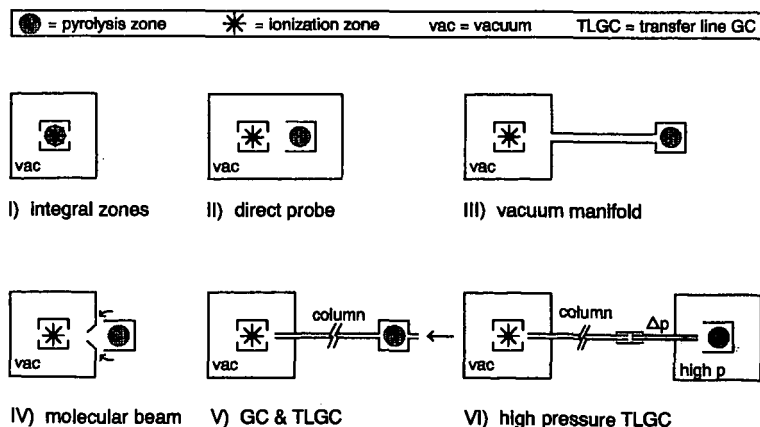


Figure 1. Schematic representation of six different pyrolysis mass spectrometry interface configurations ordered according to degree of separation between pyrolysis and ionization zones.

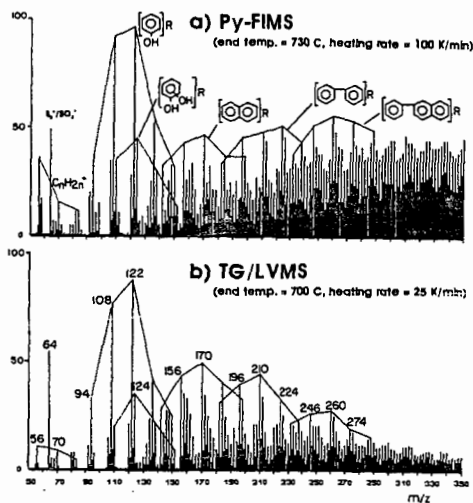


Figure 2. Comparison of mass pyrograms of hvAb Pittsburgh #8 coal obtained by (a) direct probe (100  $\mu$ g sample) Py-FIMS and (b) vacuum thermogravimetry (5 mg sample) in combination with low voltage (12 eV) EIMS (from ref. 28).

Figure 3. (a) Karhunen-Loeve ("factor") score plot for Curie-point pyrolysis mass spectra from 104 Rocky Mountain Province coals showing spontaneous separation by rank and depositional effects; (b) Chemical interpretation of the observed clustering trends (from ref. 4).

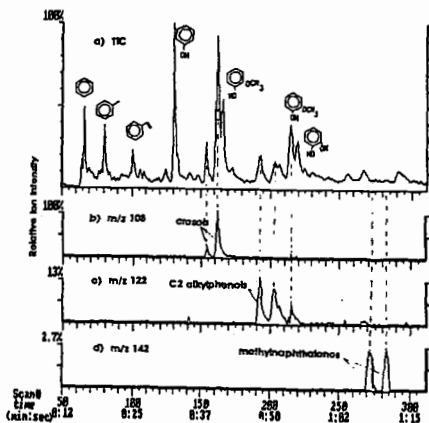
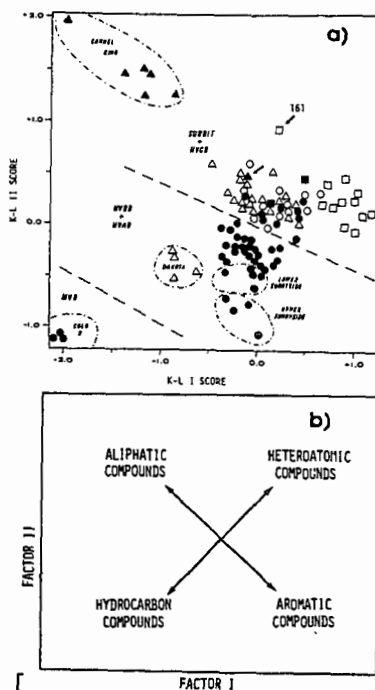


Figure 4. Typical  $\text{CO}_2$  laser pyrolysis GC/MS profile of a 100  $\mu\text{m}$  dia Beulah Zap lignite particle at 20 msec pulse duration showing effective GC separation within approx. 70 sec as well as dominant hydroxy- and methoxy-aromatic signals typical of low rank coal (from ref. 40).

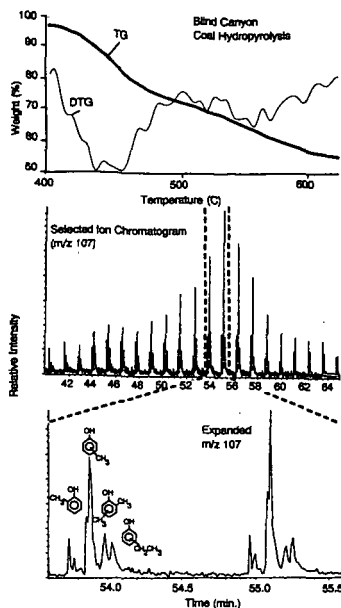


Figure 5. TG/GC/MS profiles of a 50 mg hvAb Blind Canyon coal sample in  $H_2$  at 900 psi obtained at a heating rate of 10 K/min, demonstrating feasibility of on-line GC/MS monitoring of high pressure coal conversion reactions (from ref. 41).

Figure 6. (a) Peaks containing one, two, or three oxygens from Py-HRMS of APCS #8 lignite; (b) area chart of the distribution of heteroatoms for the same coal (from ref. 17).

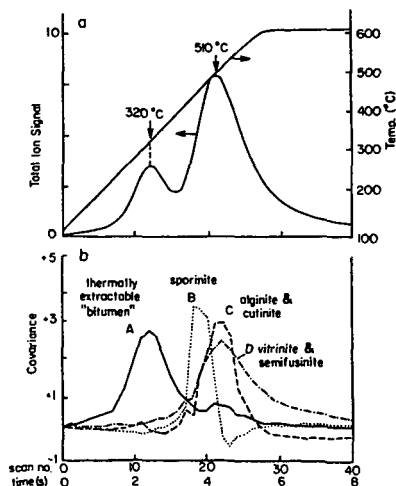
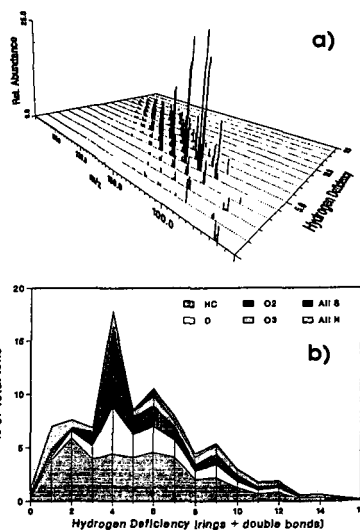


Figure 7. Time-resolved Curie-point pyrolysis MS profiles of a Pittsburgh #8 coal showing "deconvolution" of the total ion signal profile (a) into components A-D (b) by means of factor analysis techniques (from ref. 42).